

1 CORROSION CONTROL UTILIZING A HYDROGEN PEROXIDE DONOR

2
3 FIELD OF THE INVENTION

4 This invention relates to a method of inhibiting
5 corrosion as well as inhibiting scale and deposit formation
6 resulting from the saturation of mineral salts, and buildup
7 of corrosion byproducts. The invention generally relates to
8 the inhibition of corrosion of metals in contact with an
9 electrolyte and the reduction of insulating films owing to
10 scale formation/deposition. The invention most particularly
11 relates to the inhibition of corrosion on metals which
12 experience active-passive transition by application of a
13 hydrogen peroxide donor. Illustrative of such metals are
14 steel(s), aluminum, titanium or mixtures thereof; however the
15 instant invention contemplates the treatment of any metal
16 which is capable of experiencing active/passive transitions
17 when exposed to passivating agents.

18
19 BACKGROUND OF THE INVENTION

20 Corrosion of metals, particularly those metals found in
21 cooling water circulating systems, and most particularly
22 those in heat exchangers, are of critical concern.

23 In industrial cooling systems, water from rivers, lakes,

1 ponds, wells, wastewater treatment plant effluent etc., is
2 employed as the cooling media for heat exchangers. Such
3 waters can contain a variety of either dissolved and/or
4 suspended materials such as mineral salts, metals, organics,
5 silt, mud etc.

6 The cooling water from a heat exchanger is typically
7 passed through a cooling tower, spray pond or evaporative
8 system prior to discharge or reuse. In such systems, cooling
9 is achieved by evaporating a portion of the water passing
10 through the system. Because of the evaporation that takes
11 place during the cooling, both dissolved and suspended solids
12 concentrate. The concentrating of various anionic ions such
13 as chlorides and sulfates can increase the rate of corrosion
14 of the metals making up the cooling system. This is
15 especially true with the metals making up the heat exchangers
16 that are experiencing higher temperatures.

17 Furthermore, contaminants such as hydrogen sulfide can
18 also increase corrosion rates. Likewise, mineral salts, for
19 example those of calcium and magnesium can induce scaling of
20 the heat exchanger. A scale common in cooling systems is
21 calcium carbonate. Other scales or deposits such as calcium
22 phosphate or iron can also inhibit heat transfer as well as
23 induce under-deposit corrosion.

1 Deposit formation on heat exchangers seriously reduces
2 heat transfer. Corrosion byproducts can form on the metal
3 surface where a corrosion cell has formed. Deposits from
4 metal oxides, silt, mud, microbiological activity, and
5 process contamination can reduce the efficiency of heat
6 transfer as well as increase corrosion.

7 Reducing the corrosion, scaling and deposition of heat
8 exchangers and associated cooling system equipment is thus
9 essential to the efficient and economical operation of a
10 cooling water system. Excessive corrosion of the metallic
11 surfaces can cause the premature failure of process
12 equipment, necessitating down time for the replacement or
13 repair of the equipment. Additionally, the buildup of
14 corrosion products on the heat transfer surfaces impedes
15 water flow and reduces heat transfer efficiency thereby
16 limiting production or requiring downtime for cleaning.

17 Aspects of Corrosion

18 In order for corrosion to occur, a corrosion cell must
19 form. The corrosion cell consist of two half cells, the
20 cathode, and the anode.

21 The cathode is defined as the point where the reduction
22 of a reducible substance takes place. In waters where the pH
23 is greater than 4.2 (like that of a cooling water system),

1 the primary reducible substance is oxygen. The steps
2 involved with the cathode include: oxygen diffusion to the
3 metal surface, adsorb by either physical or chemical
4 adsorption, electron transfer, rearrangement with other
5 adsorbed materials (i.e. water and electrons with subsequent
6 formation of hydroxide ions), de-sorption of the newly formed
7 byproduct (hydroxide), and diffusion into the bulk meter.
8 With increased concentration of hydroxide ions, oxygen
9 diffusion and adsorption rates are reduced.

10 The anode is defined as the point where dissolution of
11 metal ions occurs. The dissolution of metal ions at the
12 anode is a chemical process. The reaction forms ferrous
13 hydroxide. Initially, the potential at the anode is low;
14 however with time, the electrical potential at the anode
15 increases. The increased potential is the result of the
16 increased concentration of metal ions (result of dissolution)
17 in the immediate vicinity of the anode. The increased
18 concentration of metal ions induces the formation of a Metal
19 Ion Concentration Cell, as well as the reduction of oxygen.
20 The increasing concentration of cationic charged ions at the
21 anode increases the electrical potential of the anode.

22 General corrosion is defined as a state where the
23 potential of the cathode decreases with time while the

1 potential at the anode increases. At some point, the
2 potentials of the cathode and anode shift or find neighboring
3 electrodes of stronger or weaker potential. This shifting or
4 jumping is the result of the mechanisms already described. As
5 the hydroxide concentration at the cathode increases, oxygen
6 adsorption decreases, and the cathodes potential goes down.
7 At the anode, where the concentration of cationic ions
8 increases, the demand for electrons increases, so the
9 potential goes up. This process of electrode reversal
10 continues across the surface of the metal resulting in a
11 uniform loss of metal.

12 Pitting corrosion refers to a condition where the
13 potential surrounding the anode is high (cathodic) and
14 electron flow is not distributed across many anodes,
15 therefore the electron comes from a local anode. Pitting
16 corrosion is of great concern because of the high loss of
17 metal from a localized area. At a metal loss rate of several
18 mils per year (MPY), general corrosion would take many
19 decades of continued corrosion before resulting in failure of
20 the part, e.g. of a heat exchanger. However, in pitting
21 corrosion, the electron flow and subsequent metal loss is
22 from a localized area. Pitting corrosion often results in
23 equipment failure long before reaching the expected life of

1 the equipment, e.g. the heat exchanger.

2 Pitting corrosion occurs when the cathodic surface has
3 been depolarized. Chlorides for example, compete for the
4 metal surface with the oxygen donor. When a chloride ion is
5 adsorbed at the metal surface, it prevents the oxygen from
6 reaching the surface. The potential at the site is reduced,
7 and the area becomes anodic. This induces a high flux of
8 electrons to flow from the localized site to the surrounding
9 cathode.

10 Passivation can be defined as the loss of chemical
11 reactivity exhibited by certain metals and alloys under
12 specific environmental conditions. The onset of passivation
13 is associated with the formation of an oxide layer that is
14 resistant to further oxidation.

15 The mechanism of passivation, as it relates to ferrous
16 metal surfaces, involves the dissolution of metal ions,
17 followed by formation of a ferrous hydroxide layer, followed
18 by conversion to an insoluble ferric oxide by reaction with
19 oxygen. Analysis of passive films indicates a layered
20 structure with an outer layer of gamma iron oxide and an
21 inner layer of magnetite.

22 Passivation occurs when we have established sufficient
23 oxidation potential. At low oxidation potential,

1 insufficient concentrations of oxidizer exist to establish a
2 homogenous oxide layer; distinct anodes and cathodes exist.
3 When sufficient oxidizer is present, the electrical potential
4 of the entire surface is increased. The concentration of
5 oxidizer is sufficient to induce the "flash" formation of an
6 oxide layer. In other words, the oxidizer concentration is
7 sufficiently high to react with the ferrous hydroxide across
8 the entire metal surface. With increased oxidation
9 potential, the current density increases. The current
10 density required to induce passivation is called the critical
11 current. At yet higher oxidizer concentrations, aggressive
12 attack of the oxide layer occurs, and the corrosion rates
13 increase; this is termed the transpassive region.

14 Passivation is a process requiring oxygen. Therefore,
15 inhibitors that induce passivation must increase the
16 oxidizing potential or make better use of the oxidizer
17 present.

18 Inhibitors such as chromate, nitrite and hydroxide
19 raise the oxidizing potential of the solution by directly
20 supplying oxygen to the anode to react with the metal ions
21 thereby reducing the formation of a metal oxide. For this
22 reason, these inhibitors can be used in solutions without
23 oxygen present. These oxidizing inhibitors are involved with

1 direct oxidation of the ferrous hydroxide to ferric oxides.

2 Inhibitors such as phosphate, silicate, borate and
3 molybdate are non-oxidizing inhibitors which form complexes
4 with iron (III) species so as to stabilize them from
5 disproportionation (the transformation of a substance into
6 two or more substances by oxidation or reduction) to the more
7 soluble Fe (II) species until reaction with dissolved oxygen
8 creates the more immune oxides. These inhibitors do require
9 the presence of oxygen to promote passivation. Their
10 performance can be enhanced with the addition of a peroxide
11 compound where peroxide is used to enhance the formation of a
12 passive oxide film.

13 Anodic inhibition is desired from an operational
14 viewpoint since the oxide film is very thin, and the
15 corrosion rates are lower than that achieved by cathodic
16 inhibition. However, the potential drawback is that if the
17 film breaks are not repaired, due to insufficient inhibitor
18 concentrations for example, rapid pitting may occur. This is
19 the result of the fact that the cathodic reaction can occur
20 all over the passive surface, but the anodic reaction (metal
21 dissolution) can only occur at broken film sites.

22 Chromate treatments have been long recognized as the
23 standard to compare other treatment programs. Chromates,

1 induce the formation of a uniform oxide film thereby inducing
2 passivation of the metal surface.

3 While chromate programs could be run at higher pH many
4 were operated at lower pH (6.5 - 7.5). This significantly
5 lowered the potential for scale formation.

6 Chromate technology has been eliminated from most
7 applications involving cooling water treatment due to the
8 environmental and human health hazards. Since the elimination
9 of chromates, the most common treatment methodologies now
10 incorporate technologies that increase scale and fouling
11 potential.

12 Anodic phosphate treatments require levels of phosphate
13 exceeding those allowed by the natural solubility of
14 phosphate when in the presence of calcium. To stabilize
15 phosphates and inhibit scale formation, polymers that
16 stabilize the formation of calcium phosphate salts are
17 applied. Also, in some areas, lower phosphate levels are
18 required to meet environmental restrictions.

19 Low phosphate levels can be achieved by incorporating a
20 cathodic inhibitor like zinc. Zinc is a cathodic inhibitor
21 that precipitates at the cathode by forming zinc hydroxide.
22 Concentrations of peroxide and peroxy-carboxylic acids can be
23 reduced with the addition of a cathodic inhibitor such as

1 zinc.

2 Again, because of the limited solubility of zinc,
3 polymers are commonly fed to help prevent fouling from
4 precipitation. Also, in many areas, zinc has environmental
5 implications.

6 Using existing treatment methods, operating cost
7 increased, and in many operating conditions such as high heat
8 flux and/or high chlorides, results are less than desirable.

9 Thus, what is needed in the industry is a treatment
10 program that is effective at inhibiting corrosion -under
11 various heat flux and water chemistry conditions, as well as
12 being environmentally innocuous.

13 DESCRIPTION OF THE PRIOR ART

14 US Patent No. 5,800,732 describes the use of hydrogen
15 peroxide as a means of controlling microbial activity in an
16 all-in-one treatment for cooling water.

17 US Patent No. 4,977,292 describes the development of an
18 organic phosphorous compound using hydrogen peroxide as an
19 oxidizer to initiate the oxidation reaction.

20 US Patent No. 5,382,367 describes the use of hydrogen
21 peroxide in cooling water systems to control microbiological
22 activity in said systems.

23 US Patent Nos. 5,980,758, 5,785,867, 5,658,467 and 5,494,588

1 describe the use of peracetic acid with nonoxidizing biocides
2 to inhibit growth of microorganisms.

3 The prior art fails to describe the use of peroxide
4 and/or peroxy-carboxylic acids as standalone corrosion
5 inhibitors, much less passivating agents, for cooling water
6 treatment. Furthermore, no prior art reference describes the
7 use of these compounds as on-line deposit control and deposit
8 removal agents for said application.

9
10 SUMMARY OF THE INVENTION

11 The instant invention is directed toward a method which
12 provides superior corrosion inhibition, particularly to those
13 areas experiencing heat transfer; namely the heat exchangers
14 where corrosion and scale potential is most prevalent. The
15 instant process recognizes the fact that both hydrogen
16 peroxide and peroxy-carboxylic acids are strong oxidizing
17 agents having important similarities to chromate (VI) in that
18 they are anionic oxidizers.

19 Since they function as anionic oxidizers, these
20 compounds have high solubility in water and readily diffuse
21 to the metal surface. Being strong oxidizers as well as
22 oxygen donors, they are able to directly supply the oxygen
23 needed to induce passivation.

1 The instant process utilizes these compounds as
2 corrosion inhibitors and passivators to achieve performance
3 equal to or exceeding that obtained by chromate. Such
4 performance has been demonstrated under high heat load
5 conditions and/or in the presence of corrosion inducing ions
6 such as chlorides. These compounds also provide an
7 environmentally innocuous treatment that eliminates the need
8 for other corrosion inhibitors such as zinc and phosphate
9 based treatments, as well as their supporting polymer
10 treatment. The instant invention teaches an innovative
11 treatment technology having application wherever removal of
12 scale or deposits in contact with an electrolyte is required.
13 The invention also teaches effective removal of insulating
14 films while inhibiting corrosion (especially under heat
15 transfer) and can be effectively used to improve operational
16 performance without suffering loss of system integrity or
17 production time.

18 The chemistry selected for removal of the insulating
19 layers is based on the composition of the deposits. In the
20 test, ferrous oxide was the primary composition and
21 therefore, peroxycitric acid solution or mineral acid was
22 affective at removing the deposit. Other chelating,
23 sequestering, and dispersing agents could also provide

1 effective results when used in conjunction with
2 peroxy-carboxylic acid(s) solutions.

3 Accordingly, it is an objective of the instant invention
4 to utilize hydrogen peroxide donors as corrosion inhibitors
5 and passivators to achieve performance equal to or exceeding
6 that obtained by chromate .

7 It is a further objective of the instant invention to
8 provide an environmentally innocuous treatment that
9 eliminates the need for other corrosion inhibitors such as
10 zinc and phosphate based treatments, as well as their
11 supporting polymer treatment.

12 It is yet another objective of the instant invention to
13 teach a treatment technology having application wherever
14 removal of scale or deposits in contact with an electrolyte
15 is required.

16 It is a still further objective of the invention to
17 teach effective removal of insulating films while inhibiting
18 corrosion (especially under heat transfer) thereby improving
19 operational performance without suffering loss of system
20 integrity or production time.

21 Other objects and advantages of this invention will
22 become apparent from the following description taken in
23 conjunction with the accompanying drawings wherein are set

1 forth, by way of illustration and example, certain
2 embodiments of this invention. The drawings constitute a
3 part of this specification and include exemplary embodiments
4 of the present invention and illustrate various objects and
5 features thereof.

6
7 BRIEF DESCRIPTION OF THE FIGURES

8 Figure 1 is illustrative of a circulating system useful for
9 conducting tests replicating a typical cooling water
10 treatment application;

11 Figure 2 illustrates a cross-sectional view of a MENTOR CHx
12 device;

13 Figure 3 is a graphical representation of Electro Chemical
14 Noise (ECN) in the presence of Chromate;

15 Figure 4 is a graphical representation of ECN in the presence
16 of Hydrogen Peroxide;

17 Figure 5 is a graphical representation of ECN in the presence
18 of Peroxide-Citric Acid;

19 Figure 6 is a graphical representation of Heat Transfer
20 During Cleaning ;

21 Figure 7 is a graphical representation of ECN During
22 Cleaning;

23 Figure 8 is a graphical representation of Activity Factor

1 (AF) During Cleaning.

2

3 DETAILED DESCRIPTION OF THE INVENTION

4 In accordance with Figure 1, a system was developed
5 incorporating the use of a heated metal element, sensors for
6 monitoring electrochemical noise corrosion, linear
7 polarization, and heat transfer efficiency. Figure 1 is
8 illustrative of a circulating system useful for conducting
9 tests replicating a typical cooling water treatment
10 application. Specifically, the instant device is comprised
11 of a system that incorporates: a MENTOR CHx heat transfer
12 device (more particularly described in Figure 2) 110 that is
13 made of the metallurgy to be tested. The metallurgy under
14 heat transfer is in contact with an electrolyte which is
15 pumped via pump 116 through a heat exchanger 112 through
16 which electrolyte from electrolyte reservoir 114 is passed.
17 The electrolyte flow rates and rates of heat transfer are
18 adjusted to desired levels by adjusting flow regulator 118.
19 A flowmeter 120 is in fluid communication for ease of
20 adjustments. If added, the concentration of a passivator is
21 measured using a standardized amperometric analyzer. A sample
22 line 124 is optionally provided for convenience in
23 withdrawing samples for testing.

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Now with further reference to Figure 2, a block 210 is comprised of a series of pieces of the desired metallurgy 212 that are joined with an insulating material 214 placed between each adjoining piece. This series of adjoined pieces will be designated the "block". A hole (not shown) is incorporated at some part of the construction process through which the electrolyte will contact the block. The metal pieces making up the block are equipped with appropriate sensing apparatus (not shown) for the sensing of ECN and LPR. Other sensing apparatus for determination of temperature gradients, heat transfer coefficients, etc. can be applied in a way that does not interfere with the performance of ECN and LPR sensing apparatus. The block is equipped with a device 216 to provide heat thru the block. The block is combined with other supporting equipment necessary for replicating the operational environment of the heat transfer equipment in question. This can include, but is not limited to, equipment necessary for replicating electrolyte flow rate, electrolyte chemical parameters, and skin temperature at the heat exchanger electrolyte interface, etc.

The process control parameters are adjusted and controlled to replicate the operational environment at the heat exchanger metal-electrolyte interface. The heated

1 element was made of 1010 carbon steel. A circulation pump was
2 attached to a reservoir pump the water of desired chemistry
3 through the testing element, a cooling coil and back to the
4 reservoir.

5 The chemistry selected for removal of the insulating
6 layers is based on the composition of the deposits.
7 Therefore, in the following tests, since ferrous oxide was
8 the primary composition, a peroxycitric acid solution or
9 mineral acid was chosen for effectively removing the deposit.
10 Other chelating, sequestering, and dispersing agents could
11 also provide effective results when used in conjunction with
12 peroxycarboxylic acid(s) solutions.

13 Water was prepared having the following chemical
14 characteristics:

15 Calcium as CaCO_3 = 110 ppm

16 Total Alkalinity as CaCO_3 = 66 ppm

17 Chloride as Cl^- = 25 ppm

18 pH = 7.9

19 The 1010 carbon steel block temperature was set to 152°F
20 which achieved a calculated skin temperature of 144°F. Flow
21 rate through the CHx was set at 3.8gpm which equates to a
22 velocity of 4ft/sec. Steady state conditions were achieved
23 and held during testing.

1 EXAMPLES:

2 Baseline - Chromate Test

3 Baseline data for chromate treatment was achieved using
4 laboratory grade sodium chromate. Initially the system was
5 treated with levels 4 times (1600 ppm) the normal
6 concentration of chromate (as CrO_4) to induce passivation.
7 After 2 hours of circulation under heat transfer, some of
8 the water was removed while it was replaced with identical
9 quality makeup water without the chromate. The operating pH
10 stabilized at 7.7 by the addition of the H_2SO_4 . This
11 dilution continued until the chromate level dropped to the
12 test concentration of (330 ppm). The system was allowed to
13 operate under steady state conditions to determine corrosion
14 rates under the described conditions as depicted in Figure 5.

15 Peroxide Test

16 The system was allowed to circulate under heat transfer until
17 it reached steady state. The water was treated with hydrogen
18 peroxide to achieve an initial dosage of 200ppm. The pH of
19 the solution was adjusted to 7.4 by the addition of H_2SO_4 .
20 After reaching steady state, the ECN was monitored and
21 recorded as illustrated in Figure 4. The system was then
22 flushed until peroxide was undetectable and the pH of the
23 circulating water equaled the flush water.

1 Figure 4 utilized the same water chemistry and heat load
2 conditions as in Figure 3, using hydrogen peroxide as the
3 corrosion inhibitor.

4 The comparative results clearly indicate the improved
5 corrosion inhibitor capability of the peroxide based
6 treatment.

7 Peroxycarboxylic Acid Test

8 Peroxycarboxylic acids are formed from acids selected
9 from the group consisting of formic acid, acetic acid, citric
10 acid, oxalic acid, gluconic acid, glucoheptonic acid,
11 succinic acid, acrylic acid, polyacrylic acid, maleic acid,
12 polymaleic acid, polyepoxysuccinic acid, ethylene-diamine-
13 tetraacetic acid, malonic acid, adipic acid,
14 phosphonobutanepolycarboxylic acid and mixtures thereof.

15 As exemplified herein, peroxycitric acid is an
16 equilibrium product of hydrogen peroxide and citric acid (a
17 "solution" of a peroxycarboxylic acid is comprised of the
18 peroxycarboxylic acid, hydrogen peroxide and the carboxylic
19 acid). A solution of peroxycitric acid was prepared by
20 combining a solution of citric acid, with 30% laboratory
21 grade hydrogen peroxide. The ratio of the blend was 2:1
22 hydrogen peroxide to citric acid based on actives.

23 After flushing the system, 130ppm of the blend was added

1 to the water. The pH was measured at 6.8. After allowing
2 the system to reach steady state, the ECN corrosion rate was
3 monitored and recorded as illustrated in Figure 5.

4 The results illustrate that hydrogen peroxide and
5 peroxy-carboxylic acids (and/or respective constituents
6 thereof) provide superior corrosion inhibition compared to
7 the long established industry standard chromate based
8 treatment technology.

9 Cleaning Test

10 To achieve a skin temperature of 144°F, the CHx required
11 65.6412 BTU/hr.ft² x 10³. This was recorded as the baseline
12 heat transfer under steady state conditions. The CHx was then
13 exposed to a corrosive electrolyte under stagnant conditions
14 for several days.

15 When the circulation pump was activated, red water was
16 observed leaving the CHx. After allowing the system to reach
17 steady state under heat transfer, the rate of heat transfer
18 required to achieve a skin temperature of 144°F was monitored
19 and recorded as 52.8664 BTU/hr.ft² x 10³.

20 The lower heat transfer value indicates a 19.46%
21 reduction in heat transfer efficiency due to the presence of
22 corrosion byproducts (ferric oxide).

23 The electrolyte was initially treated with 1000ppm of a

1 peroxycitric acid solution made from a 2:1 actives weight
2 ratio of hydrogen peroxide and citric acid. Figure 6
3 illustrates the heat transfer increased (data point 4) while
4 ECN (Figure 7) showed a corresponding rise in corrosion rate.
5 ECN corrosion rates then dramatically drop (data point 5),
6 followed by the onset of a passive-steady state condition
7 (data points 8-13).

8 By data point 12 (Fig. 6), heat transfer recovered 22%
9 of the lost heat transfer resulting from the removal of much
10 of the insulating ferric oxide.

11 Data point 13 shows the affects of adding 1000ppm of HCl
12 (based on active(s)). Heat transfer is completely restored
13 while maintaining unprecedented control of ECN corrosion rate
14 and Activity Factor (Figure 8). The "Activity Factor" (AF)
15 is calculated using the equation:

16
$$AF = \sigma_i / i_{rms}$$

17 where σ_i is the standard deviation of the electrochemical
18 current noise data, and i_{rms} is the root mean square of the
19 electrochemical current noise. The AF detects changes in
20 current and highlights the deviation from the steady state
21 condition.

22 Test results clearly illustrate the cleaning and

1 corrosion inhibition capabilities of peroxycarboxylic acid
2 solutions. Even in the presence of high chlorides and low pH
3 (~4.0), pitting corrosion was averted, and corrosion rates
4 were controlled while regaining 100% efficiency.

5 This technology can also be utilized in conjunction with
6 other corrosion inhibitors to improve their performance.
7 Examples of such other corrosion inhibitors include but are
8 not limited to orthophosphates, polyphosphates, phosphonates,
9 zinc and azoles. It is further understood that the instant
10 treatment technology could, and in many cases would be
11 utilized with other water treatments such as deposit control
12 agents, corrosion inhibitors and microbiological control
13 agents.

14 It is to be understood that while a certain form of the
15 invention is illustrated, it is not to be limited to the
16 specific form or arrangement of parts herein described and
17 shown. It will be apparent to those skilled in the art that
18 various changes may be made without departing from the scope
19 of the invention and the invention is not to be considered
20 limited to what is shown and described in the specification
21 and drawings.